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XEROX

SOLAR REGENERATIVE CHEMICAL SYSTEM

Report No. 4

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Project No. 3A99-09-001
Task No. 3A99-09-001-04
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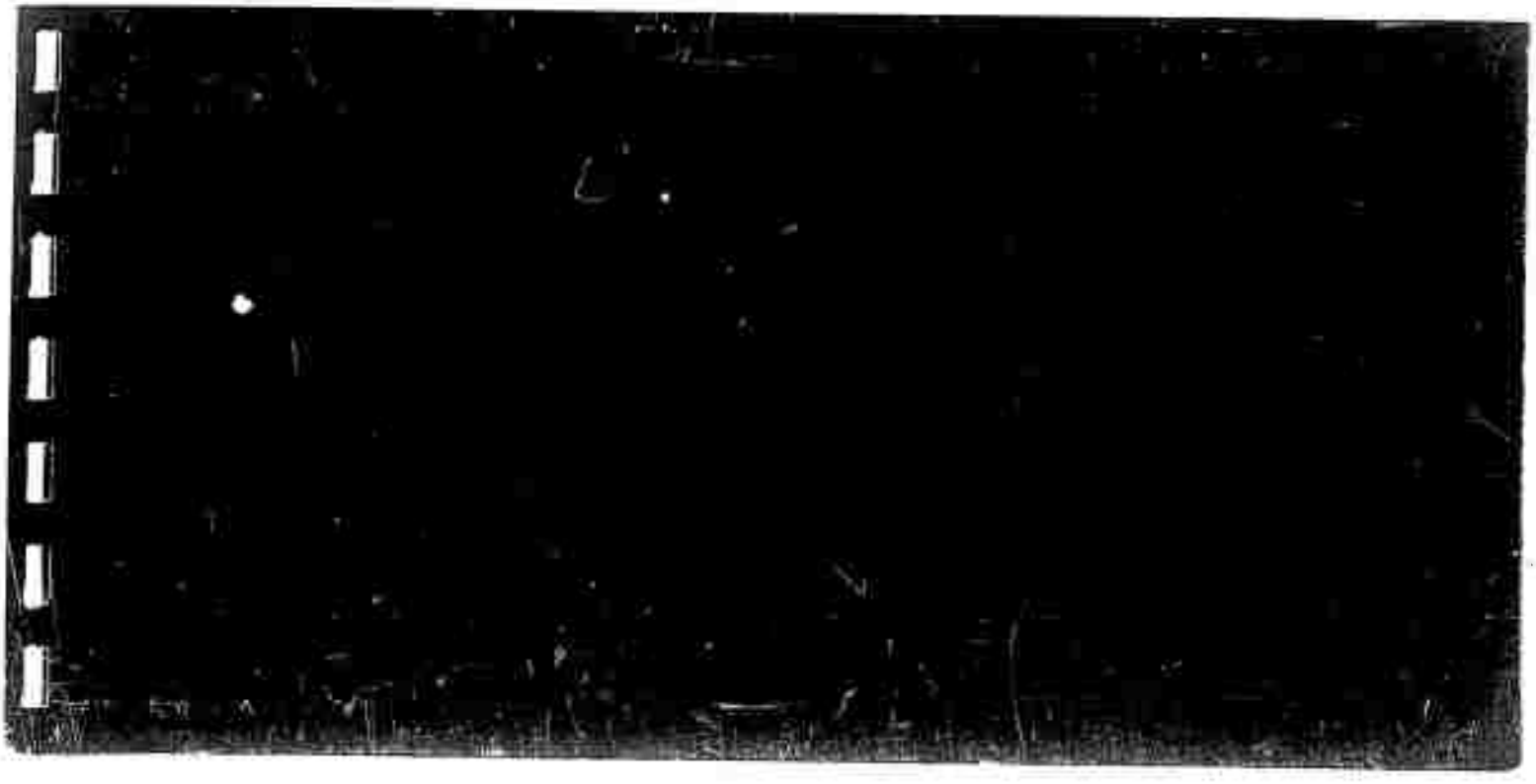

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Project No. 3A99-09-001
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Fourth Semiannual Report, 1 Jan 1961 – 30 June 1961

Object: Development of a Solar Regenerative Fuel Cell

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Approved:

M. Eisenberg
Manager, Electrochemistry

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Lockheed Aircraft Corporation
Missiles and Space Company
Sunnyvale, California

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Section 1
PURPOSE

This project is concerned with the study of the conversion of solar energy into electrical energy by means of closed-cycle chemical systems in the form of regenerative fuel cells.

Solar energy may be used either in the form of thermal energy or as electromagnetic radiation (photons) to reverse the direction of a normally spontaneous reaction. This project has been divided into two separate tasks. Task A deals with thermally regenerative systems, and Task B deals with photochemically regenerative systems.

1.1 TASK A, THERMALLY REGENERATIVE SYSTEMS

The program under Task A has been directed toward a study of the properties of the cadmium, iodine chemical system for use in a closed-cycle system. In such a cycle, the cell reactants Cd and I_2 are regenerated from the cell product Cd I_2 in a thermal reactor heated by an external energy source, e.g., solar energy or nuclear energy.

As pointed out by de Bethune (Ref. 1) and Eisenberg (Ref. 2), the desirable thermodynamic properties for a regenerative fuel cell reaction are as follows:

- A negative free energy, ΔF_a, for the fuel cell reaction
- A large negative entropy
- ΔC_p as close to zero as possible

As reported earlier (Ref. 3), ΔF at 500° K for the reaction

$$Cd + I_2 \rightarrow Cd\,I_2$$

is -45.9 kcal, $\Delta S_{500^\circ K}$ = -28 eu (subsection 4.1.2). The value of ΔC_p has not been calculated for this process.

Because of the apparent advantages of the CdI_2 system, the experimental program has been concerned with a study of this compound. Phase 1 is concerned with theoretical considerations of thermodynamics and kinetics. Phase 2 is an experimental program on the electrochemical characteristics of the fuel cell. Phase 3 is a study of the high-temperature decomposition of CdI_2. Phase 4 will be an attempt to build a complete experimental regenerative system.

1.2 TASK B, PHOTOCHEMICALLY REGENERATIVE SYSTEMS

Task B is directed to the study of photochemically active systems for use in closed-cycle fuel cell systems and is concerned with bulk effects or photogalvanic effects rather than surface or photovoltaic effects. The experimental program is designed to study the effect of the parameters of the system on the photoinduced electrochemical effects and the efficiency of energy conversion.

Phase 1 is an exploratory program designed to discover photosensitive chemical systems and includes investigation of water soluble dyes, insoluble dyes and inorganic materials. Phase 2 is the study of the kinetics of the reactions involved, and Phase 3 is the assembly and study of experimental regenerative systems.

Section 2
ABSTRACT

The effect of temperature, pressure, and electrolyte composition on the CdI_2 fuel cell are reported and the thermodynamic significance discussed. A power density of 56 mw/cm^2 of anode area and 126 mw/cm^2 of cathode area was obtained. The $\Delta E/\Delta T$ was measured and the entropy change calculated.

The studies on photoregenerative chemical systems included the exploration of insoluble organic dyes and inorganic complexes as well as the more usual water-soluble dyes. The insoluble dyes proved to be very advantageous. The rates of reaction and the magnitude of the photopotentials are much improved. Spectra, quantum efficiencies, and the effect of wavelength, light intensity, temperature, and electrolyte composition on the photoinduced properties are reported for one of the insoluble dye systems. A two cell experimental regenerative system has been operated for 90 days.

The effect of halide salts on the quantum efficiency of photobleaching of the proflavin-ascorbic acid system is reported and discussed.

Photopotentials of some Werner-type complexes were measured.

Section 3
PUBLICATIONS, LECTURES, REPORTS, AND CONFERENCES

3.1 PUBLICATIONS AND LECTURES

H. Silverman, W. Momyer, and M. Eisenberg, Solar Regenerative Galvanic Cells, Part II. Presented by W. Momyer at the XVth Annual Power Sources Conference, Atlantic City, N. J., 9 May 1961.

3.2 CONFERENCES

J. Murphy, of Army Signal Research and Development Laboratory, and M. Eisenberg, J. Inkster, and H. Silverman of Lockheed Missiles and Space Division met 22 and 23 March 1961 to discuss future objectives of the project. It was suggested that greater emphasis be placed on the thermal regenerative system. Since that time, a TWX has been received requesting phasing out of the photochemical research by 1 September 1961.

Section 4
FACTUAL DATA

4.1 TASK A, THERMALLY REGENERATIVE SYSTEM

The purpose of Task A is to carry out research on systems, which may be suitable for use in thermally regenerative galvanic systems. On the basis of preliminary thermodynamic calculations (Ref. 3), the cadmium, iodine system appeared most promising.

The experimental program under this task is concerned with

- A study of the electrochemical parameters of a fused-salt cell based upon the reaction

$$Cd + I_2 \rightarrow Cd\,I_2$$

- A study of the effect of temperature and pressure on the operation of the cell
- A study of the effect of the electrolyte composition on the cell behavior
- A study of the thermal decomposition of $Cd\,I_2$

The experimental program has thus far been concerned with those parameters most likely to affect the operation of a fused-salt fuel cell, i.e., temperature, pressure, and electrolyte composition, as well as an analysis of the results.

4.1.1 Experimental Procedures

All chemicals are reagent grade, vacuum dried, and stored in a dessicator until used. The fused-salt fuel cell apparatus was described in a previous report (Ref. 3). All measured potentials are referred to a Cd, $Cd\,I_2$ electrode. The apparatus designed for the study of the high-temperature decomposition of $Cd\,I_2$ is shown in Fig. 1.

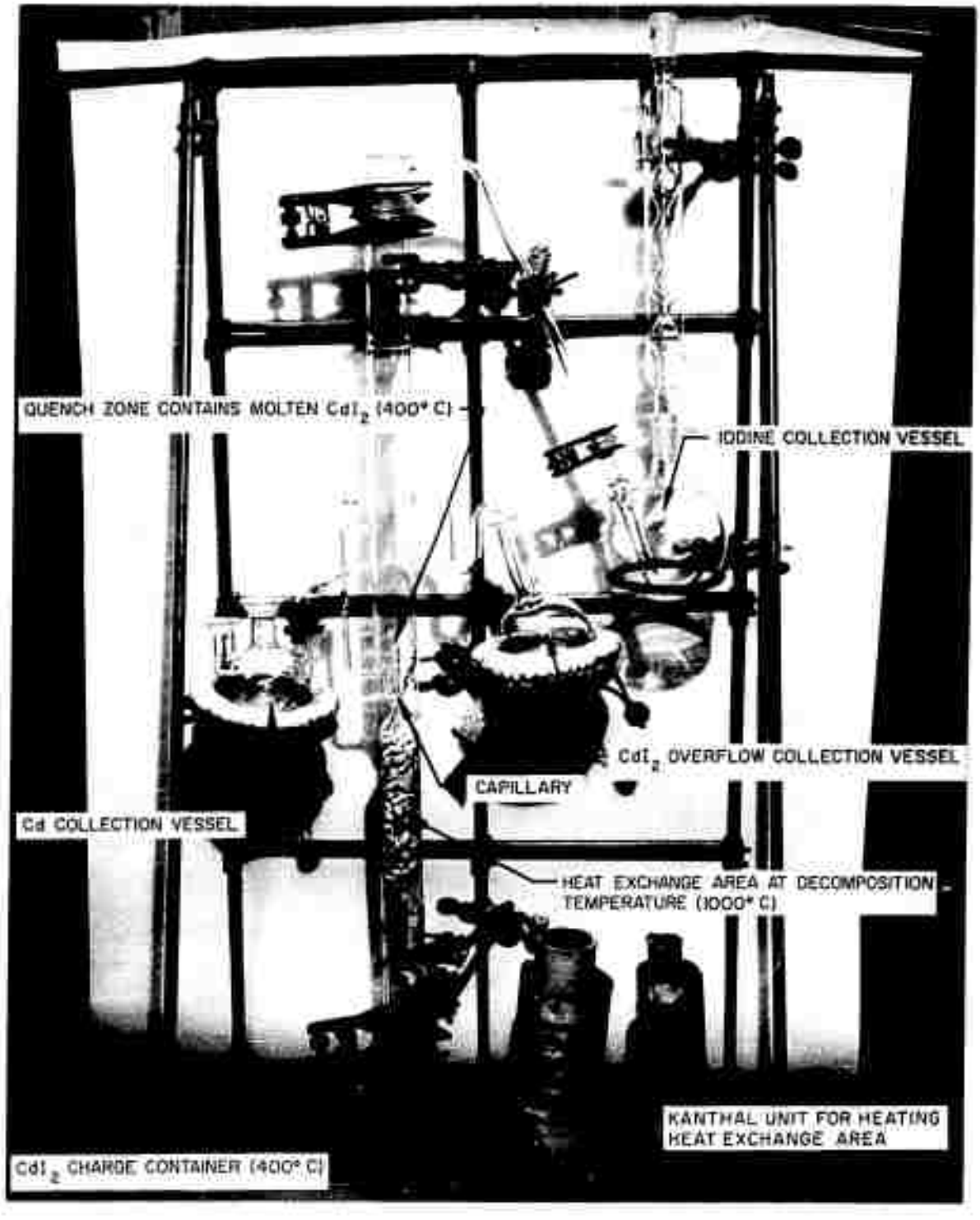


Fig. 1 Apparatus for Studying Decomposition of CdI_2

The $Cd\ I_2$ is contained in a vessel from which it is vaporized into the heat exchanger maintained at 1000°C by a Kanthal heating element. The gases pass up through a capillary and into a quench zone. The quench bath is molten $Cd\ I_2$. The condensed metal settles to the bottom of the heat exchanger and quench zone and eventually overflows into the collection vessel. The iodine is trapped in a vessel and the excess $Cd\ I_2$ overflows into another, from which it may be returned to the charge container.

4.1.2 Effect of Temperature on the Cadmium, Iodine Galvanic System

Open-circuit voltage and current-potential curves were obtained for cadmium, iodine fuel cells operated over a temperature range from 370°C to 480°C. The variations of the cell voltage at open circuit and the cell voltage and electrode polarization at a current density of 50 ma/cm^2 with temperature are shown in Table 1. A plot of the open-circuit voltage and cell voltage at 50 ma/cm^2 as a function of the absolute temperature is shown in Fig. 2.

It can be seen that as the temperature increases, the open-circuit voltage and polarization decrease until at about 520°C (793°K) there is virtually no polarization at a current density of 50 ma/cm^2. Unfortunately, at this temperature, the electrolyte and the cadmium metal become so miscible that it is difficult to maintain the cadmium as a separate layer.

The $\Delta E/\Delta T$ obtained from the slope of the plot of open-circuit voltage (OCV) versus temperature is -0.458 mv/deg. Since

$$\left(\frac{\partial \Delta F}{\partial T}\right)_p = -\Delta S$$

and

$$\Delta F\ (cal\ ) = -E \cdot n \cdot 23{,}060$$

Table 1

EFFECT OF TEMPERATURE ON THE ELECTROCHEMICAL CHARACTERISTICS OF THE Cd I_2 CELL[a]

Run	Temp (°C)	Zero Current	50 ma/cm^2		
		Cell Voltage (v)	Cell Voltage (v)	Anode Polarization (v)	Cathode Polarization (v)
43	370	0.882	0.38	> 0.40	> 0.40
44	370	0.888	0.28	> 0.40	> 0.40
55	415	0.875	0.50	0.48	0.10
58	415	0.867	0.40	> 0.40	0.08
61	480	0.841	0.70	0.06	0.10
65	480	0.842	0.70	0.09	0.06

(a) Iodine Pressure: 31 in. Hg

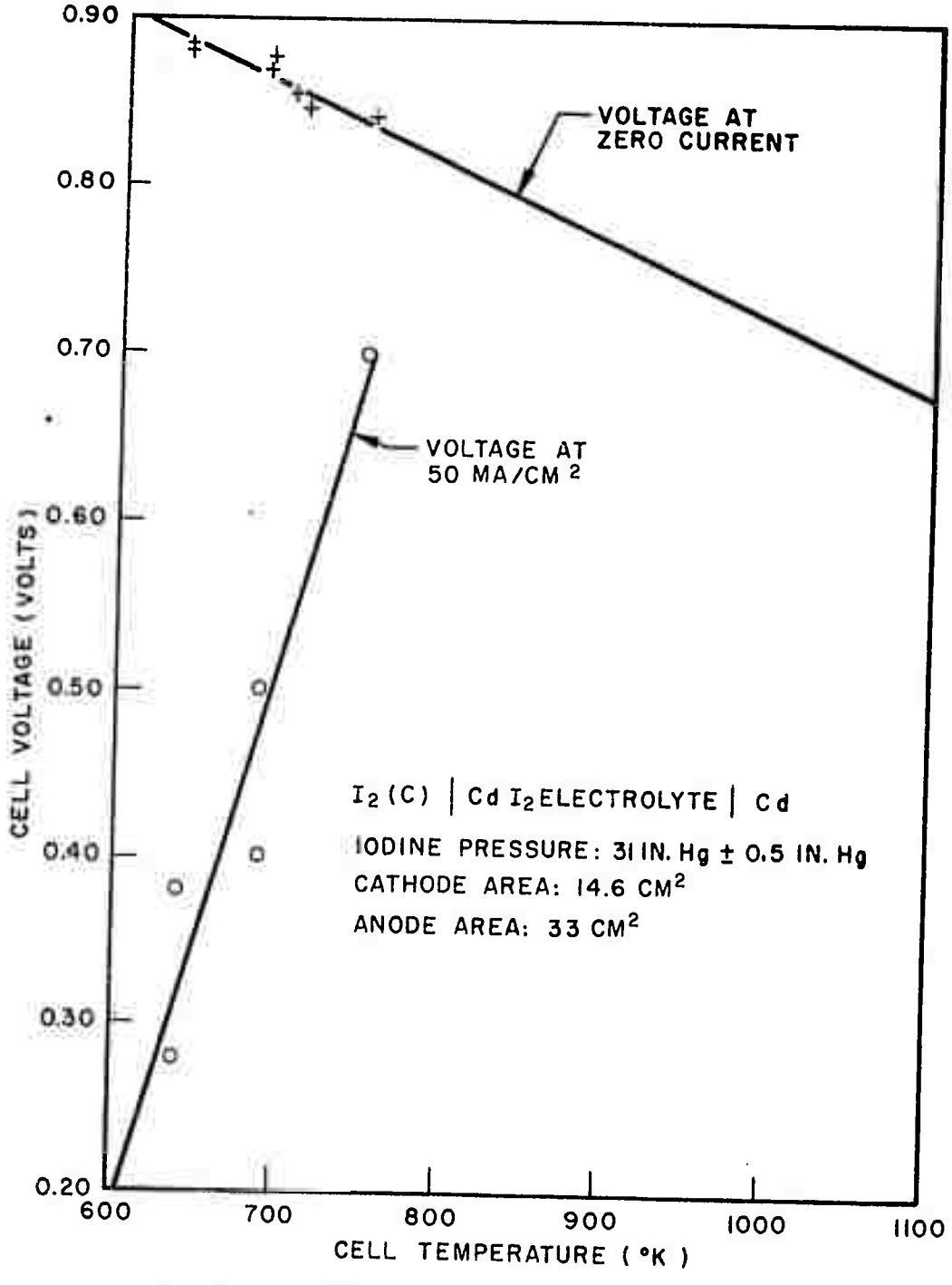


Fig. 2 The Effect of Temperature on Cell Voltage

Then

$$\frac{\partial \Delta F}{\partial T} = - \frac{\partial \Delta E}{\partial T} \cdot n \cdot 23,060 = -\Delta S$$

or

$$-\Delta S = 0.458 \cdot n \cdot 23,060$$

$$\Delta S = -21.2 \text{ eu}$$

The value of the function

$$\frac{\Delta F - \Delta H_{298}}{T}$$

for the reaction

$$Cd\,(s) + I_2\,(g) \rightarrow Cd\,I_2\,(s) \qquad (i)$$

has been estimated to be 33.3 cal at 700°K (Ref. 4) and ΔH_{298} is reported to be -63 kcal. Thus, $\Delta F_{700°K}$ is calculated to be -40.0 kcal. The emf of the reaction V_r is given by the relation

$$V_r = - \frac{\Delta F}{n \mathcal{F}}$$

and is equal to 0.87 volts at 700°K compared to the measured value of 0.86 volts uncorrected for activities. By rearrangement of the Gibbs-Helmholtz equation it can be shown that

$$\Delta S = \left(\frac{\partial (n \mathcal{F} V_r)}{\partial T} \right)_p$$

The entropy change at 25°C, ΔS_{298}, for the reaction

$$Cd(s)_{298} + I_2(g)_{298} \rightarrow Cd\,I_2(s)_{298}$$

is reported to be -35.1 (Ref. 4).

The entropy change for the reaction

$$Cd(\ell) + I_2(g) \rightarrow Cd\,I_2(\ell)$$

is obtained by summing the following processes:

$$Cd(\ell)_{700°} \rightarrow Cd(s)_{298} \qquad \Delta S = -8.13 \text{ eu (Ref. 5)}$$

$$I_2(g)_{700°} \rightarrow I_2(g)_{298} \qquad \Delta S = -7.62 \text{ eu (Ref. 5)}$$

$$Cd\,I_2(s)_{298} \rightarrow Cd\,I_2(\ell)_{700°} \qquad \Delta S = 23.1 \text{ eu}$$

This last value is estimated from the value of the entropy change in raising the temperature to 1000°K $S_{1000°} - S_{298}$, reported by Quill (Ref. 4) to be 32 eu, and correcting for the entropy change in cooling from 1000°K to 700°K by the equation

$$\Delta s = \int_{1000°}^{700°} C_p \frac{dT}{T}$$

C_p is estimated to be approximately equal to that of $Hg\,I_2$ or 25.0 (Ref. 4). The overall entropy change is calculated to be -27.8 eu. While this is appreciably larger than the experimental value of -21.2 eu reported above, it must be remembered that deviations from unit activity were not corrected. Since a large temperature coefficient of free energy is a desirable property in a regenerative system (Ref. 3), this entropy value is encouraging.

4.1.3 Effect of Pressure on the Cadmium, Iodine Galvanic System

Without changing the electrode or the electrolyte, the applied iodine pressure was varied and the effect on the operating characteristics of the cadmium, iodine fuel cell was determined. As expected, the anode potential was unaffected while the cell voltage and cathode polarization, as shown in Fig. 3, were found to optimize with increasing pressure.

Pressure has two major effects on the operation of a fuel cell: It affects the reversible potential of the gas diffusion electrode, where changes in pressure will affect the fugacity of the volatile components of the electrode. Since this effect is a function of the logarithm of the pressure

$$E = E_o - \frac{RT}{n\mathcal{F}} \ln p_i \ ,$$

little effect on the reversible potential would be expected over the range of pressure studied. The second effect is a kinetic effect and depends upon the physics of porous electrodes and the kinetics of transport processes. These problems have been discussed by Justi and co-workers (Ref. 6) and Eisenberg (Ref. 7). The quantitative aspects are beyond the scope of this work. However, it can be qualitatively deduced that as the pressure increases, the number of active pores in the porous electrode will increase and the gas side concentration polarization will decrease. The net result is a decrease in polarization at a given current density with increasing applied pressure. However, as the pressure continues to increase, the number of active pores will pass through a maximum (Ref. 3), and the polarization will increase again. Thus, a plot of polarization versus pressure should exhibit a minimum, which is dependent upon the pore structure of the electrode. It is apparent from the results shown in Fig. 3 that the optimum pressure has not been reached.

4.1.4 Effect of the Cd I_2 Concentration on the Electrolyte on the Cadmium, Iodine Galvanic System

Polarization data were obtained at 410° C and an iodine pressure of about 32 in. Hg for cadmium, iodine fuel cells as a function of the concentration of cadmium iodide in the

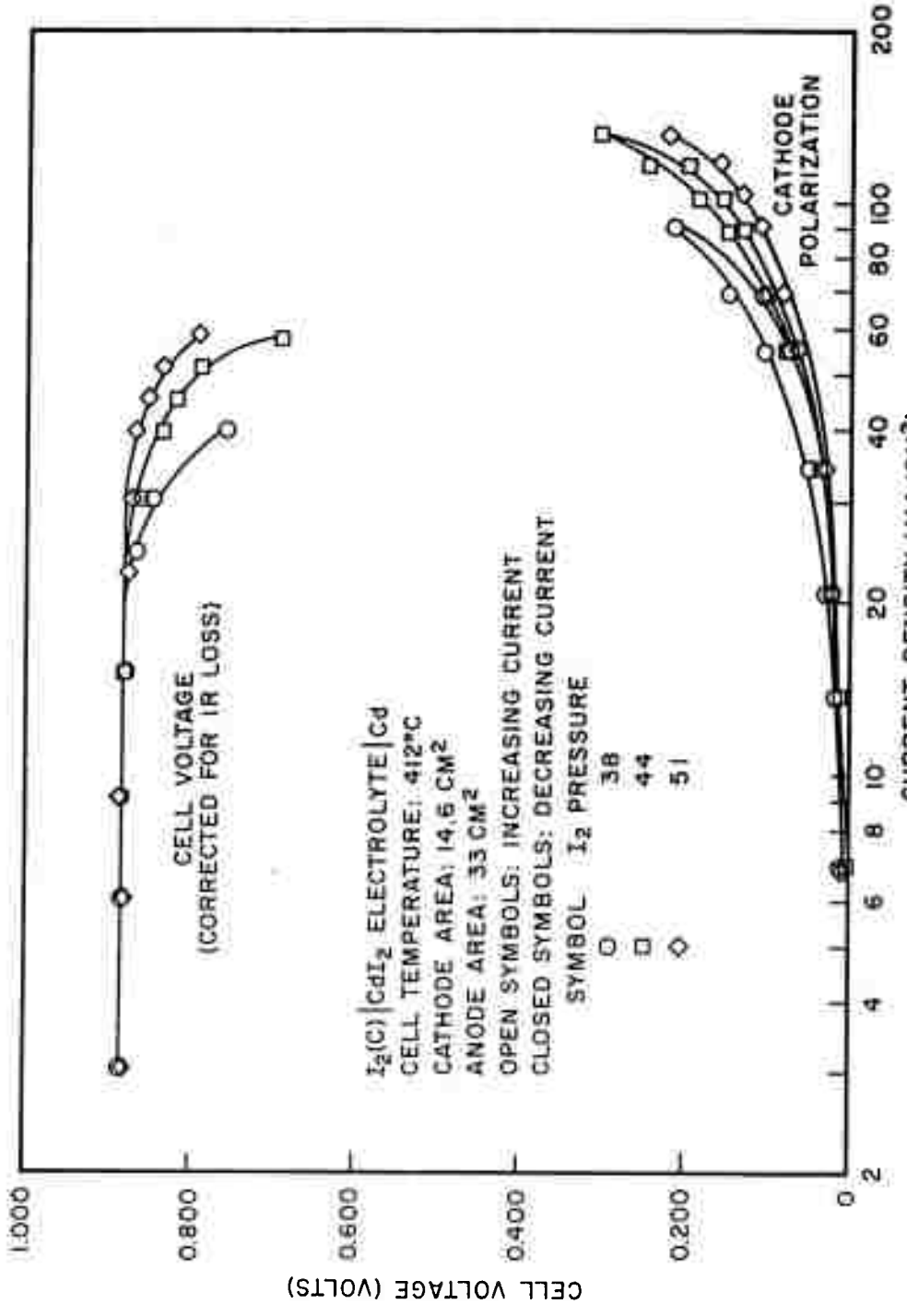


Fig. 3 Cathode Polarization and Cell Voltage as a Function of Iodine Pressure

electrolyte. The results obtained are summarized in Table 2. The results indicate that the open-circuit voltage of the cell remains fairly constant at 0.869 ±0.007. However, it is apparent from Fig. 4 that at a current density of 50 ma/cm^2 the cell voltage goes through a maximum at approximately 65 mole percent cadmium iodide. These results are as expected and are explained as follows.

The variation of concentration of the Cd I_2 would not be expected to change the thermodynamic or open-circuit cell voltage appreciably, since this varies only as the log of the concentration. However, as the composition of the electrolyte deviates from the eutectic or minimum melting point composition, it would be expected that the viscosity of the electrolyte would increase and the mobility of the ions decrease. This is reflected by an increase in concentration polarization. Further, since Cd I_2 is only slightly ionized, it is a relatively poor conductor. As a result, the resistance of the electrolyte at 85 mole percent Cd I_2 is appreciably higher.

4.1.5 Qualitative Results on Decomposition Studies

The batch-type thermal regenerator used for the study of the decomposition of Cd I_2 is illustrated in Fig. 1. Initially, this apparatus was assembled with opaque quartz pebbles. However, on heating, the opaque quartz absorbed heat and expanded faster than the vycor and the vycor tube was shattered. The apparatus was reassembled with vycor helices and was successfully heated and cooled without any mishap. A small amount of iodine was collected, but before any quantitative results could be obtained a power failure caused the vycor tube to crack.

4.2 TASK B, PHOTOCHEMICALLY REGENERATIVE SYSTEMS

This task, concerned with photoregenerative galvanic systems, has, until recently, concentrated on soluble organic dyes. The main feature of the work during this report period has been the study of inorganic photosensitive chemicals and insoluble dyes deposited on inert electrodes.

Table 2

EFFECT OF THE CONCENTRATION OF CADMIUM IODIDE IN THE ELECTROLYTE ON THE CdI_2 CELL[a]

Run	CdI_2 Concentration (mole %)	Open Circuit Voltage (v)	Current Density (50 ma/cm^2)			Cell Resistance (Ω)
			Cell Voltage (v)[b]	Anode Polarization (v)	Cathode Polarization (v)	
HT-87	50	0.879	0.52	0.10	0.03	0.082
HT-88	50	0.875	0.80	0.14	0.03	0.093
HT-67	60	0.865	0.85	0.11	0.01	0.092
HT-68	60	0.853	0.85	0.08	0.04	0.084
HT-69	60	0.858	0.84	0.07	0.05	0.089
HT-84	75	0.865	0.82	0.07	0.01	0.051
HT-85	75	0.875	0.81	0.08	0.04	0.069
HT-86	75	0.865	0.84	0.08	0.04	0.100
HT-79	85	0.875	0.68	0.10	0.07	0.102
HT-81	85	0.875	0.62	0.16	0.09	0.126
HT-82	85	0.875	0.76	0.13	0.08	0.134

(a) Temp 412° C; Iodine pressure 31 in. Hg

(b) Corrected for IR drop

(c) Anode area: 33 cm^2; Cathode area: 14.6 cm^2; Cell voltage is recorded at cathode current density indicated

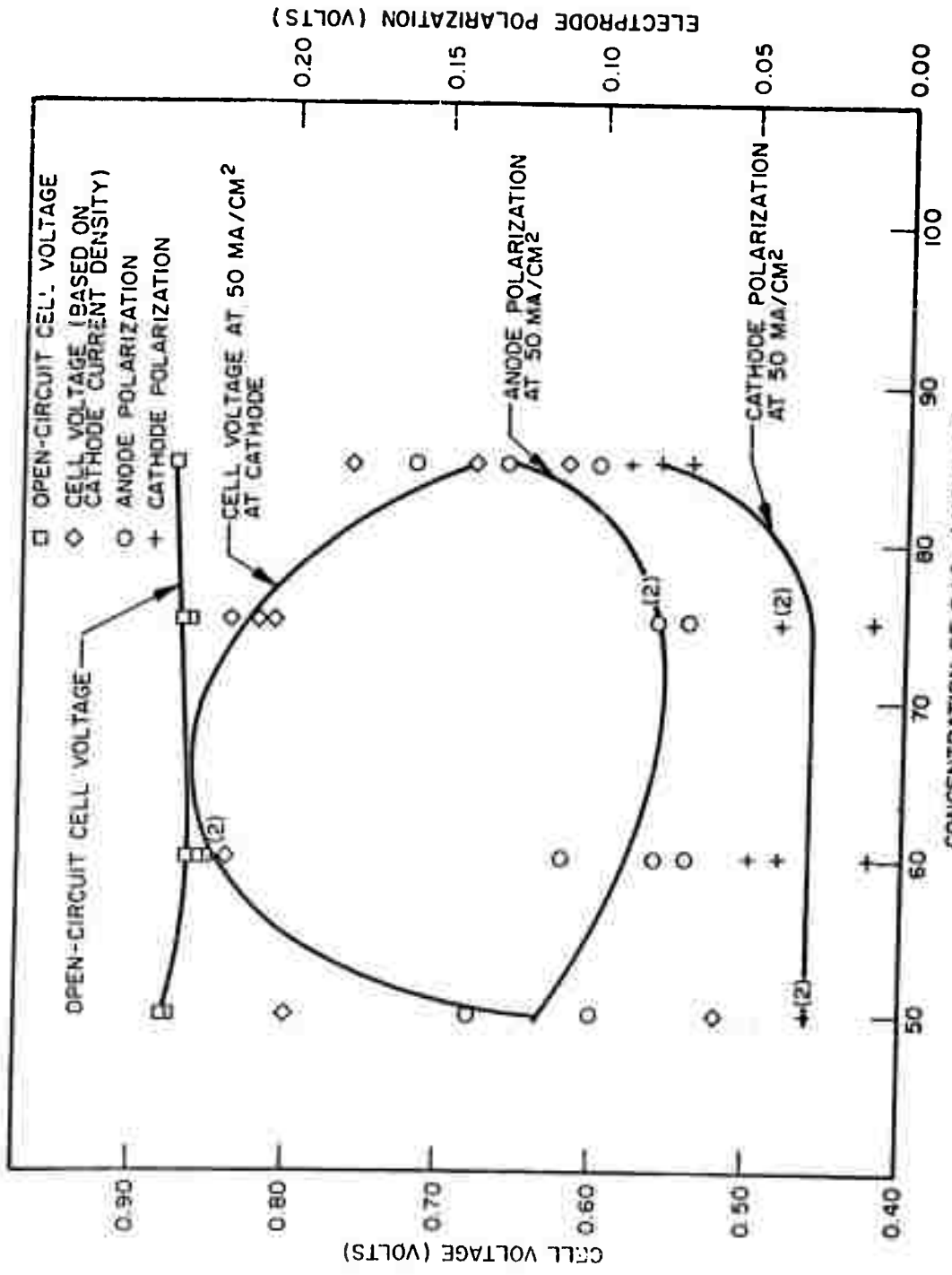


Fig. 4 Characteristics of the CdI_2 Cell as Function of CdI_2 Concentration

The success achieved with heterogeneous photosensitive elements has caused a major shift of effort from water-soluble dyes although some work to complete various facets of the research with water-soluble dyes was performed.

4.2.1 Dye-Coated Electrodes

A heterogeneous photosensitive chemical system where the photosensitive chemical exists in the solid state offers several advantages. The major advantage is the increased activity of the dye. Deposited on the electrode, the dye has unit activity. In solution, the activity is limited by the solubility of the dye and is about 10^{-3}M. Other advantages are that the dye is isolated and therefore does not interfere in the subsequent reaction in the dark cell, the diffusion path of the photoactive species is much shorter, and high quantum efficiencies have been reported for systems of this type (Ref. 8).

The properties of a dye-coated electrode dipping into an electrolyte may be likened to a p-n junction type of solar cell. The dye is considered to be a p-type semiconductor and the electrolyte with reducing agent n-type. The losses of efficiency may now be compared to that of a solar cell. Kleinman (Ref. 9) and Wolfe (Ref. 10) assigned losses of efficiency in solar cells to the following:

- Reflection losses. This is a surface effect and with dye systems is probably very low.
- Absorption of only part of the solar spectrum.
- Utilization of only part of the energy of the incident photon in the excitation step. Only those photons whose energy is equivalent to the threshold energy can be completely utilized. Energy in excess of that needed to excite the electron is dissipated as heat.
- Incomplete collection of the current carrying particle. Applied to the dye system this is due to radiative decay or collision with foreign particles before reaction with the reducing agent can take place.

- Junction loss, the difference between the theoretical energy gap and the observed open-circuit voltage, is due to diffusion of charges across the p-n junction.
- Resistive losses

Experimental procedures. In general, the procedures were as described in previous semiannual reports (Ref. 3). The special techniques used to study dye-coated electrodes are described below.

The coated electrodes were prepared by dipping a platinum foil electrode, which had previously been fired to a red heat, into a saturated methanol solution of the dye. The electrode was then dried in air.

Working electrodes for use in screening experiments were prepared by dipping silver screen into molten silver chloride. All solutions were deaerated unless otherwise noted.

The quantum efficiencies of electron production were measured using a 596-mμ interference filter between the light source (Ref. 3) and the electrode. The intensity of the incident radiation was measured with a calibrated Eppley thermopile connected to a Hewlett-Packard microvolt ammeter. The fraction of light absorbed was calculated by the relationship

$$a = (1 - T)(1 + rT)$$

where T is a measured quantity obtained by eluting the adsorbed dye from the electrode in a measured volume of methanol and measuring the fraction of light transmitted with a Beckman DK-2 Spectrophotometer, and r is the reflectance of bright platinum. The current flow was measured with a Weston microammeter. The ratio of faradays/sec emitted to einsteins/sec absorbed is the quantum efficiency.

The reflectance spectrum was measured by means of the apparatus sketched in Fig. 5. The absorbance of the dye on the platinum was determined by the relationship

$$\frac{I_\phi(\text{dye})}{I_\phi(\text{Pt})} = \text{fraction of reflected light}$$

$$= \frac{\text{ammeter deflection due to light reflected from coated Pt}}{\text{ammeter deflection due to light reflected from bare Pt}}$$

where $I_\phi(\text{dye})$ is the intensity of the light reflected from the dye-coated surface and $I_\phi(\text{Pt})$ the intensity of light reflected from the bare platinum surface.

$$\log \frac{I_\phi(\text{dye})}{I_\phi(\text{Pt})} = -\mathcal{E}\,l$$

where $\mathcal{E}$ is the absorbancy of the dye and l is the thickness of the dye coating.

The wavelength dependence of the photoinduced properties was determined by calibrating the power output of a Bausch and Lomb monochromator as a function of wavelength. A Bell and Howell projector was used as the light source and the emergent energy was measured with a calibrated Eppley thermophile. Both the exit and entrance slits of the monochromator were wide open to maximize the intensity of light emerging from the monochromator. The experiments were carried out by replacing the thermopile with a cell oriented so that the emerging light was incident on the dye-coated electrode. Current and potential were measured as a function of wavelength.

The intensity dependence of the photoinduced properties was measured by introducing a series of neutral gray filters between the projector and the electrode. The light intensity was measured with the thermopile and the current and potential recorded at each intensity.

Power experiments were performed as described previously.

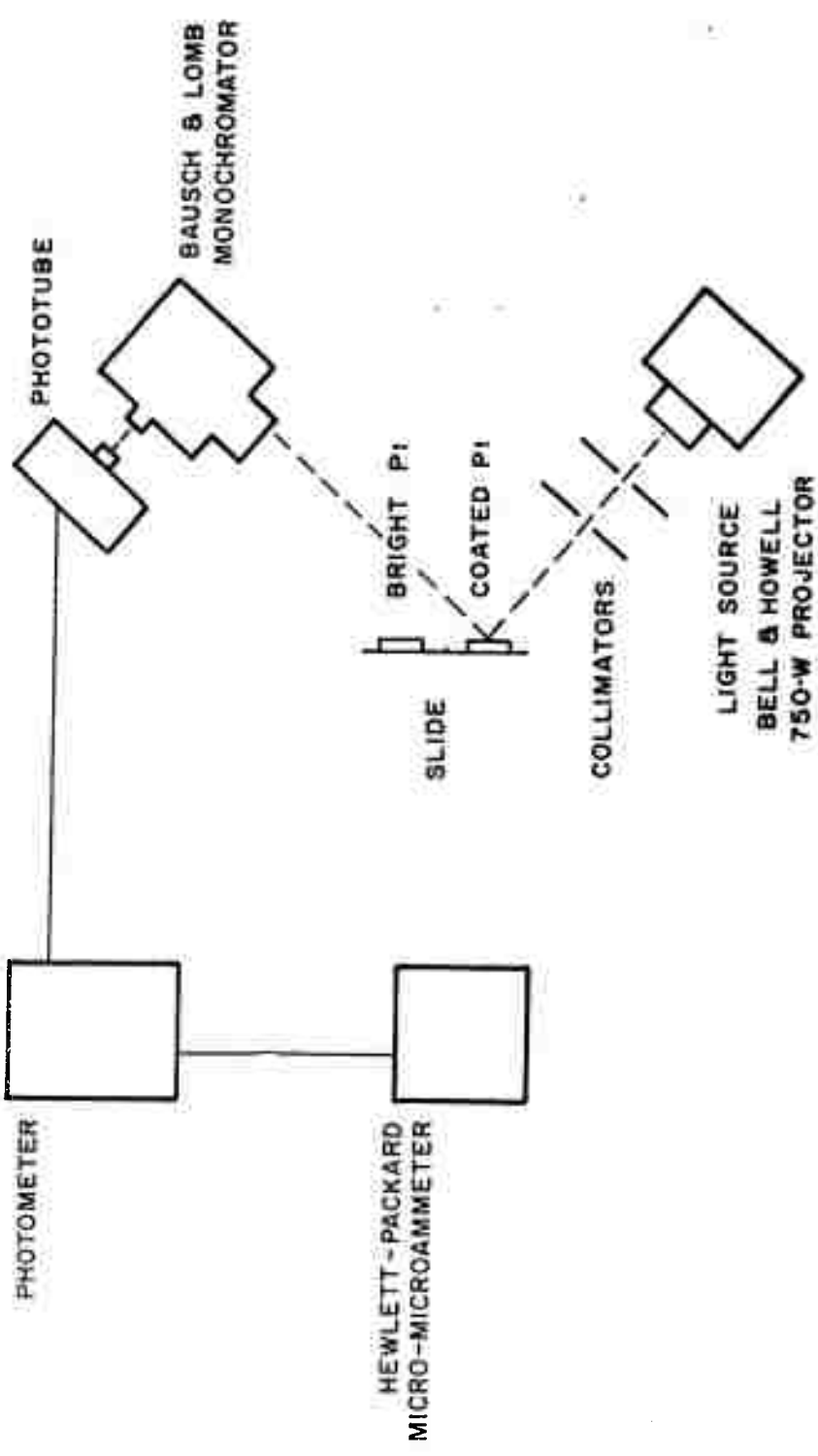
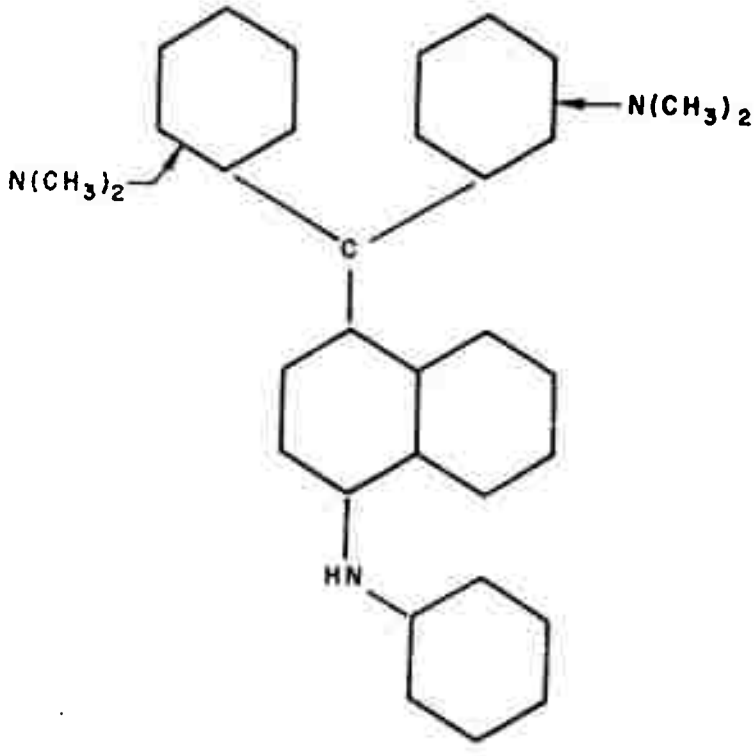


Fig. 5 Schematic of Apparatus Used for Measuring Reflectance Spectra

Spectra of Victoria Blue B. The large majority of experiments with dye-coated electrodes used Victoria Blue B (VBB), a waxoline dye with the structure



Absorption spectra of Victoria Blue B dissolved in methanol and of Victoria Blue B deposited on glass as well as a reflection spectra of dye deposited on platinum were measured. The spectra are reproduced in Fig. 6. The notable features of these spectra are the broadening of the absorption peak when the dye is absorbed on glass, and the shift of 15 mμ toward the red for the reflectance spectrum.

The spectra exhibit fairly wide absorption bands in the visible and the dye will probably absorb from 25 to 40 percent of the sun's incident energy (Ref. 11).

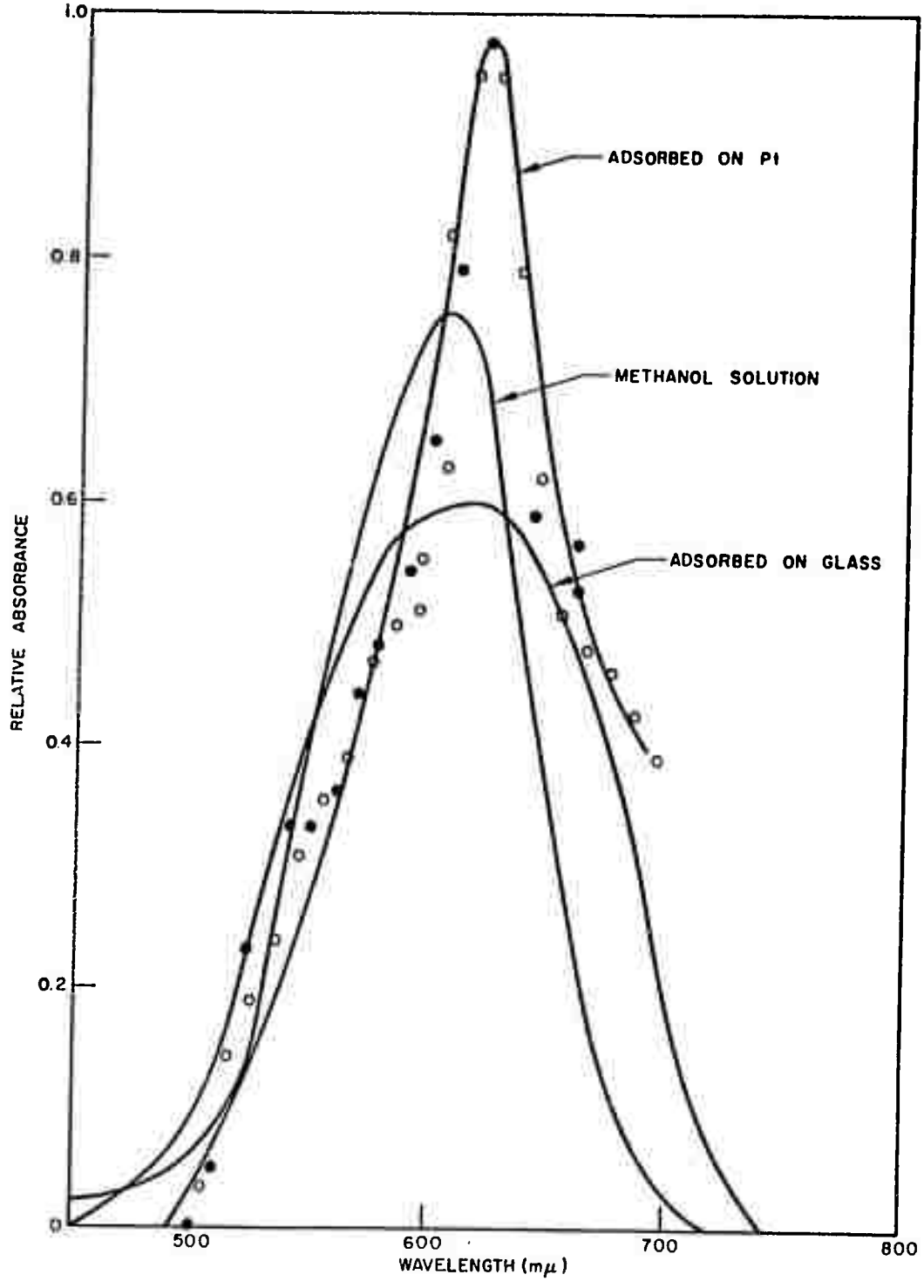


Fig. 6 Spectra of Victoria Blue B

The threshold wavelength is about 700 mμ. The energy content of 1 mole of quanta, which is an einstein, is given by the relation

$$Nh\nu = \frac{2.86 \times 10^4}{\lambda\,(m\mu)} \text{ kcal}$$

where N is Avogadro's number, ν is the frequency of light, and h, Planck's constant (6.624×10^{-27} erg sec). Thus at 700 mμ, 1 einstein is equivalent to

$$\frac{2.86 \times 10^4}{700} = 40.8 \text{ kcal}$$

The voltage equivalent of this energy is given by

$$\mathcal{E} = \frac{40.8 \text{ kcal}}{n \cdot \mathcal{F}}$$

where n is the electron exchange per molecule and $\mathcal{F}$ the faraday (-23.060 kcal/volt equivalent). Assuming a 1-electron change the maximum photopotential, i.e., change of potential due to absorption of light quanta, to be expected is approximately 1.8 volts assuming a thermodynamically reversible reaction.

Measured photopotentials range around 0.450 volts or about 10.4 kcal. Part of this loss is represented by the difference in energy levels between the ground state of the dye and the reducing agent and also the difference between the excited singlet state and the metastable triplet state to which the dye decays before reacting. Other losses involved were discussed above. The efficiency of energy absorption is $\frac{10.4}{40.8} \times 100$ or about 25 percent.

Effect of electrolyte composition. Dye-coated electrodes, in contrast to results obtained with soluble dyes, exhibit large photopotentials in the absence of reactive species in the electrolyte. Thus, a VBB-coated platinum electrode will develop a photopotential of about 0.4 volts at pH 7.0 in a deaerated solution (dark potential = 0.240 volts and photoinduced

potential = -0.192 volts versus Ag/Ag Cl electrode). However under these conditions only negligible currents could be obtained.

The addition of various inorganic redox couples were found to influence the direction and the magnitude of the photopotential of VBB-coated electrodes as shown in Table 3. The dark potential follows the standard potential of the inorganic reagent, while the photopotential and the photoinduced potential pass through maximum values. The maxima are apparently the result of an appreciable dark reaction between Eu^{++} and VBB as evidenced by a large dark current, and resulting in the reduction of some of the dye. It will be interesting to see the effect of reducing reagents with intermediate standard potentials between Eu^{++} and Sn^{++}.

For the systems described in Table 3, only Sn^{++} resulted in appreciable photocurrents. However, on repeated cycling of this system, the photocurrent and the photopotential decreased. Indeed, when equimolar solutions of Sn^{++} and Sn^{++++} were used, the result was a rapid irreversible photobleaching of the dye. This suggests that the buildup of Sn^{++++} upon repeated cycling causes an irreversible bleaching of the dye.

The failure of inorganic couples led to an investigation of ascorbic acid. At pH 1.0, ascorbic acid did not produce any appreciable current, probably because the dissociated acid is required for reaction. However, when the pH was increased to above 4, this reagent proved to be very effective. Since dehydroascorbic acid, the assumed product of the photochemical reaction, is known to undergo an irreversible hydrolysis above pH 5 (Ref. 13), further investigation of this system was restricted to pH 4.0.

Concentration of ascorbic acid. Increasing the concentration of ascorbic acid was found to increase both the photopotential and the photocurrent. As shown in Fig. 7, both the dark potential and the photoinduced potential increase logarithmically with the concentration of the ascorbic acid. However, the absolute slope of the photoinduced potential, -50 mv/log $\left[H_2A\right]$, where $\left[H_2A\right]$ is the concentration of the ascorbic acid,

Table 3

THE PHOTOPOTENTIAL OF VICTORIA BLUE B-COATED ELECTRODES WITH VARIOUS INORGANIC REAGENTS

Reagent[a]	Standard Potential E° (v)[b]	Dark Potential[c] E°_o (v)	Photoinduced[c] Potential E°_* (v)	Photopotential[d] E°_ϕ (v)
$Cr_2O_7^=$	-1.10	0.705	0.765	0.060
Fe^{++}	-0.77	0.360	0.330	-0.030
Cu^+	-0.15	0.130	-0.047	-0.177
Sn^{++}	-0.07	0.041	-0.385	-0.426
Eu^{++}	+0.43	-0.320	-0.335	-0.015

(a) Concentration in all cases was 1×10^{-2} M/l of species indicated plus trace of oxidized form or reduced form. The pH was 1.0

(b) Ref. 12

(c) Potentials versus Ag, AgCl

(d) $E^\circ_\phi = E^\circ_* - E^\circ_\phi$

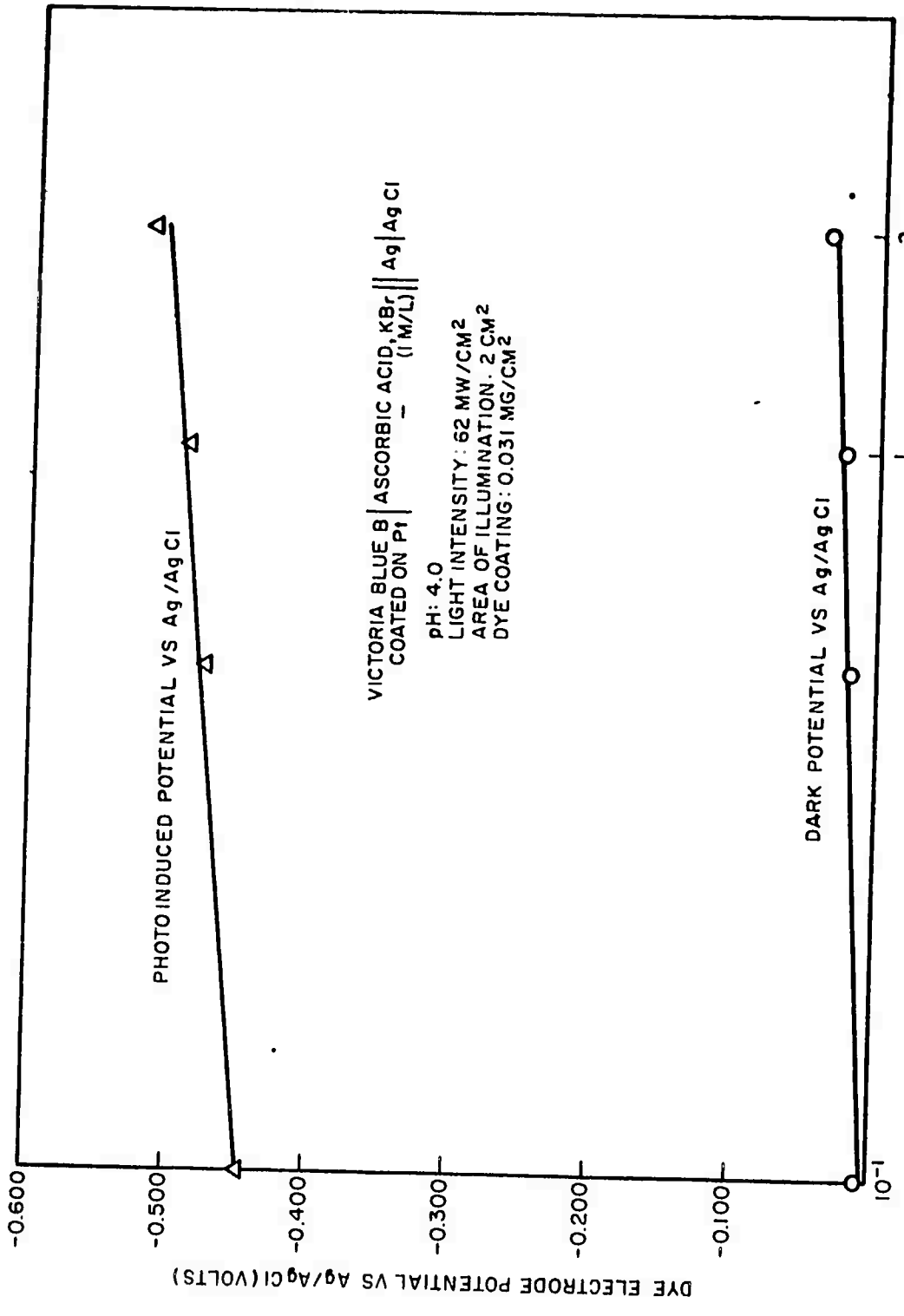


Fig. 7 Dark Potential and Photoinduced Potential of Victoria Blue B-Coated Electrodes as a Function of Ascorbic Acid Concentration

is larger than that of the dark potential -25 mv /log $\left[H_2A\right]$. The net result is an increase in the photopotential. The slopes would also indicate that the potential determining step in the light is a 1-electron change involving ascorbic acid while that in the dark is a 2-electron change assuming that the potential dependence on the ascorbic acid concentration is represented by a relationship similar in form to the Nernst equation, e.g.,

$$E = K \cdot \frac{RT}{n\mathcal{F}} \ln Q$$

or its dertvative at 25°C

$$\frac{\partial E}{\partial \ln Q} = \frac{59 \text{ mv}}{n}$$

holds, where E is the measured potential, K is a constant related to the standard potential, and Q is a functioning of the concentration of ascorbic acid, n, R, $\mathcal{F}$, and T have their usual meanings.

In Fig. 8, current-potential curves for the VBB-coated electrodes as a function of ascorbic acid concentration are shown. The differences in the curves observed at low current density merely reflect the variation of the zero current potentials of the electrode with concentration as shown in Fig. 11. While at the limiting current, there is little difference between the curves except at a 0.1 M/l concentration where the limiting current is appreciably smaller. These current-potential curves indicate that concentration polarization of some kind is limiting the current output.

Effect of temperature. An Arrhenius plot of current at a fixed load versus temperature is shown in Fig. 9. The linear results show that the current increases with temperature according to the equation

$$I = I_o e^{-\Delta E/RT}$$

where ΔE is the activation energy and the other symbols have their usual meaning.

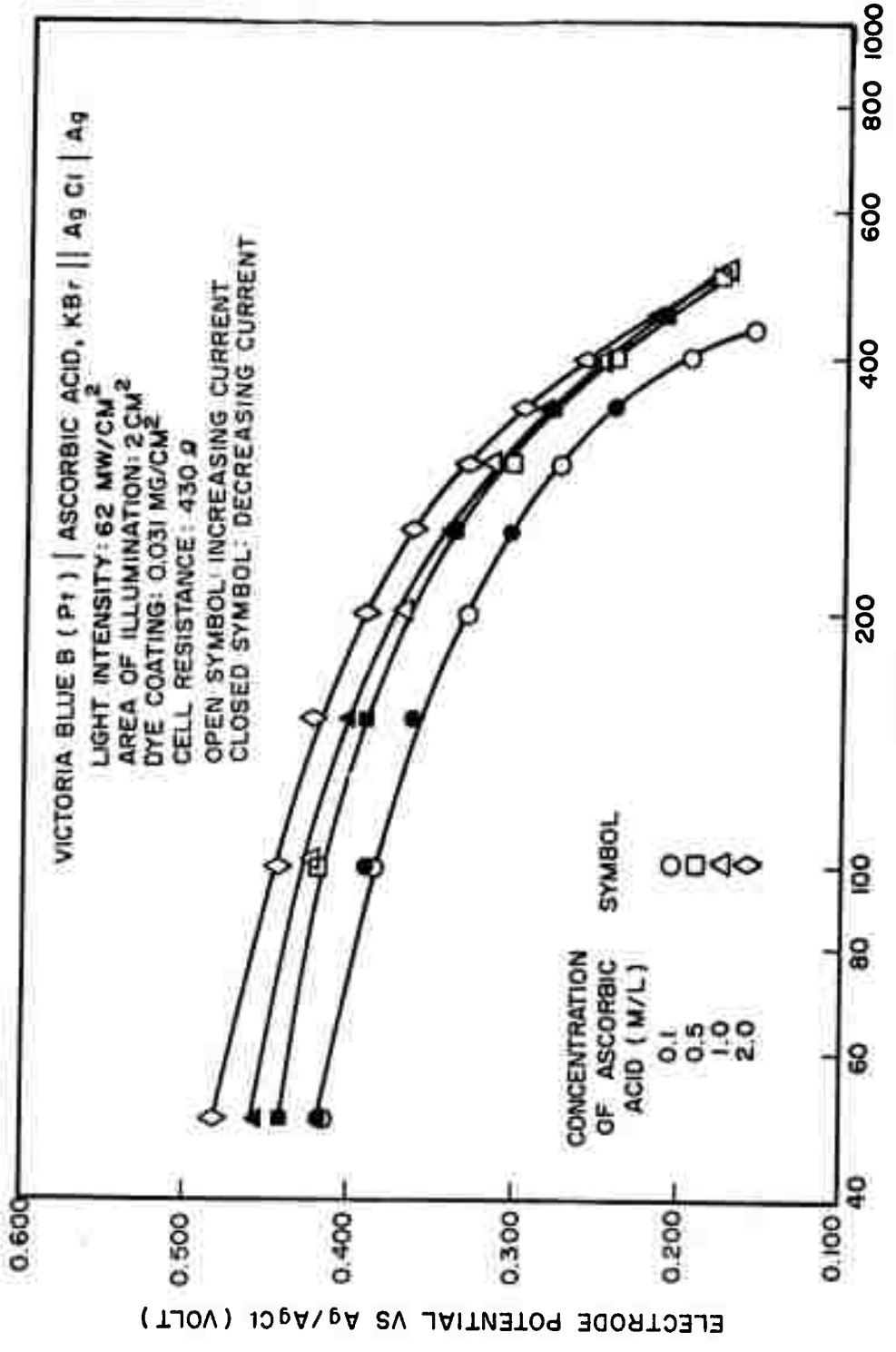


Fig. 8 Effect of Ascorbic Acid Concentration on Current-Potential Curves for the Victoria Blue B-Coated Electrode

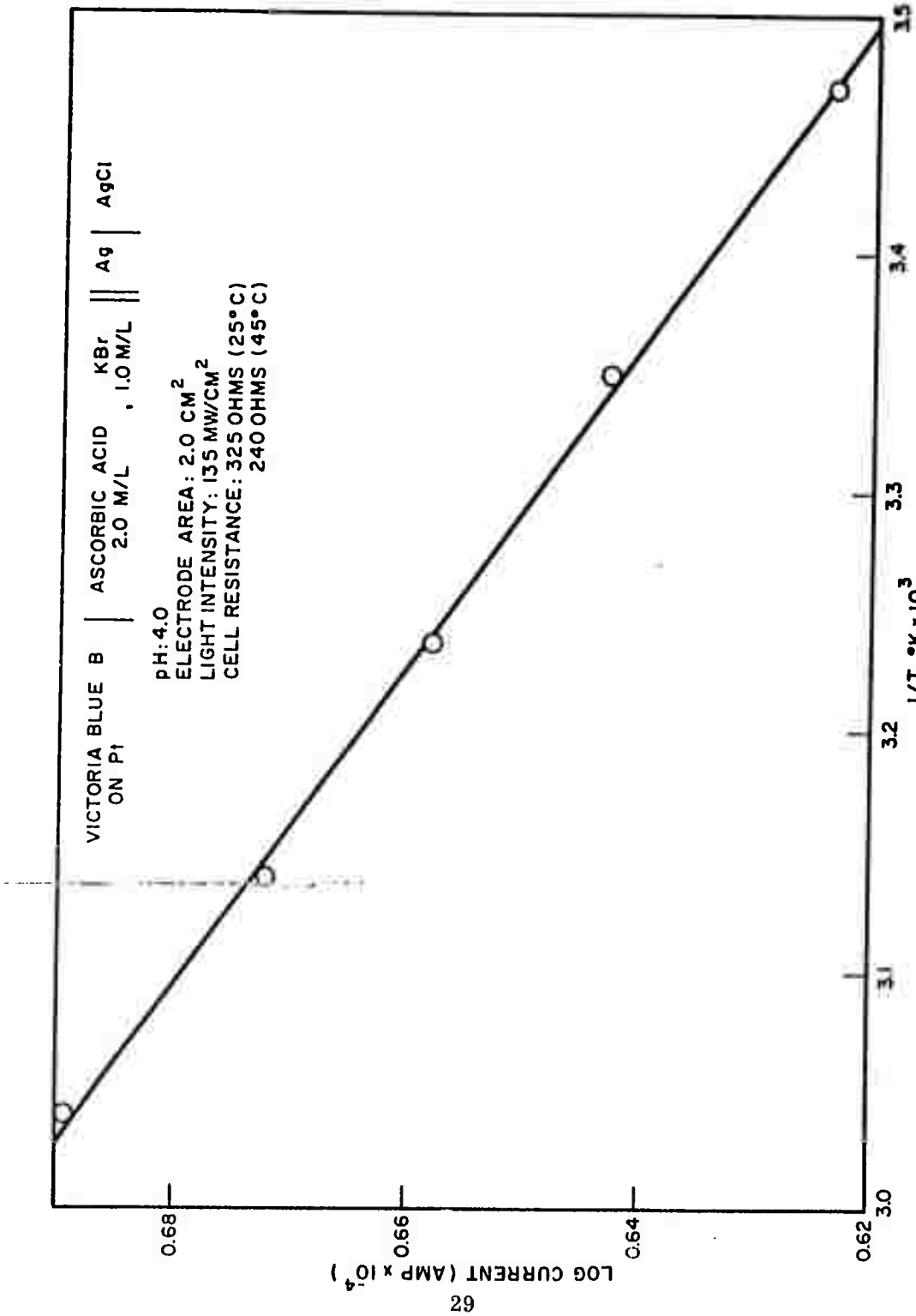


Fig. 9 Effect of Temperature on Current for the Victoria Blue B-Coated Electrode – Ascorbic Acid System

The activation energy calculated from the slope of Fig. 9 is 350 cal. The rather small increase in current with temperature is more likely due to the change in conductivity of the electrolyte than any other factor.

The photoinduced potential, E_*, over the same range of temperatures changed 1.2 mv/deg. Since

$$\Delta S = -n\mathcal{J}\frac{\partial(E_*)}{\partial T}$$

Then

$$\Delta S = -1 \times 23,060 \times 1.2 \times 10^{-3}$$

$$\Delta S = -28 \text{ eu}$$

Since

$$\Delta F = \Delta H - T\Delta S$$

and

$$\Delta F_{\text{measured}} = 10.4 \text{ kcal}$$

Then

$$\Delta H_{298} = 10,400 - 298\,(55)$$

$$= 18,650$$

and the maximum efficiency of the fuel cell, $\frac{\Delta F}{\Delta H}$ (2), is equal to approximately 55 percent. This efficiency is further limited by the factors discussed previously and the

fact that this is a regenerative cycle and should have a Carnot-type efficiency (Refs. 1 and 2), the upper and lower temperatures being calculated from the equivalent black-body radiation of the light source and the operating temperature of the cell. A complete discussion of the Carnot cycle as applied to photovoltaic effects is beyond the scope of this report but is adequately presented by A. Rose (Ref. 14).

Wavelength dependence. The photoinduced potential and thus the photopotential were found to be independent of wavelength. This confirms the threshold theory, which states that the incident quanta must contain sufficient energy to excite the electron and any energy above this value is wasted. However, the current and therefore the power output is a direct function of the rate at which quanta is absorbed and therefore should be a function of intensity and the percent of the incident energy absorbed. As shown in Fig. 10, the relative power conversion,

$$\text{Relative Power Conversion} = \frac{\text{Power Conversion}}{\text{Max Power Conversion}} = \frac{\frac{\text{(Current) (Potential)}}{\text{Incident Power}}}{\text{Max Power Conversion}},$$

follows closely the absorption spectrum.

Light intensity dependence. Light intensity was expected to have two effects. The limiting current was expected to have a linear dependence on intensity and the open-circuit steady-state concentration of the electrode active material was expected to increase with intensity resulting in a logarithmic change in the zero current potential.

Figure 11 shows the variation of the logarithm of the current as a function of the logarithm of the light intensity. The current is shown to increase linearly up to a light intensity of 100 mw/cm^2. The leveling off or saturation current is probably a complex function involving many variables which have not yet been evaluated for this process.

The variation of the photopotential as a function of the logarithm of the light intensity is shown in Fig. 12. It can be seen that the photopotential is a monotonic function of

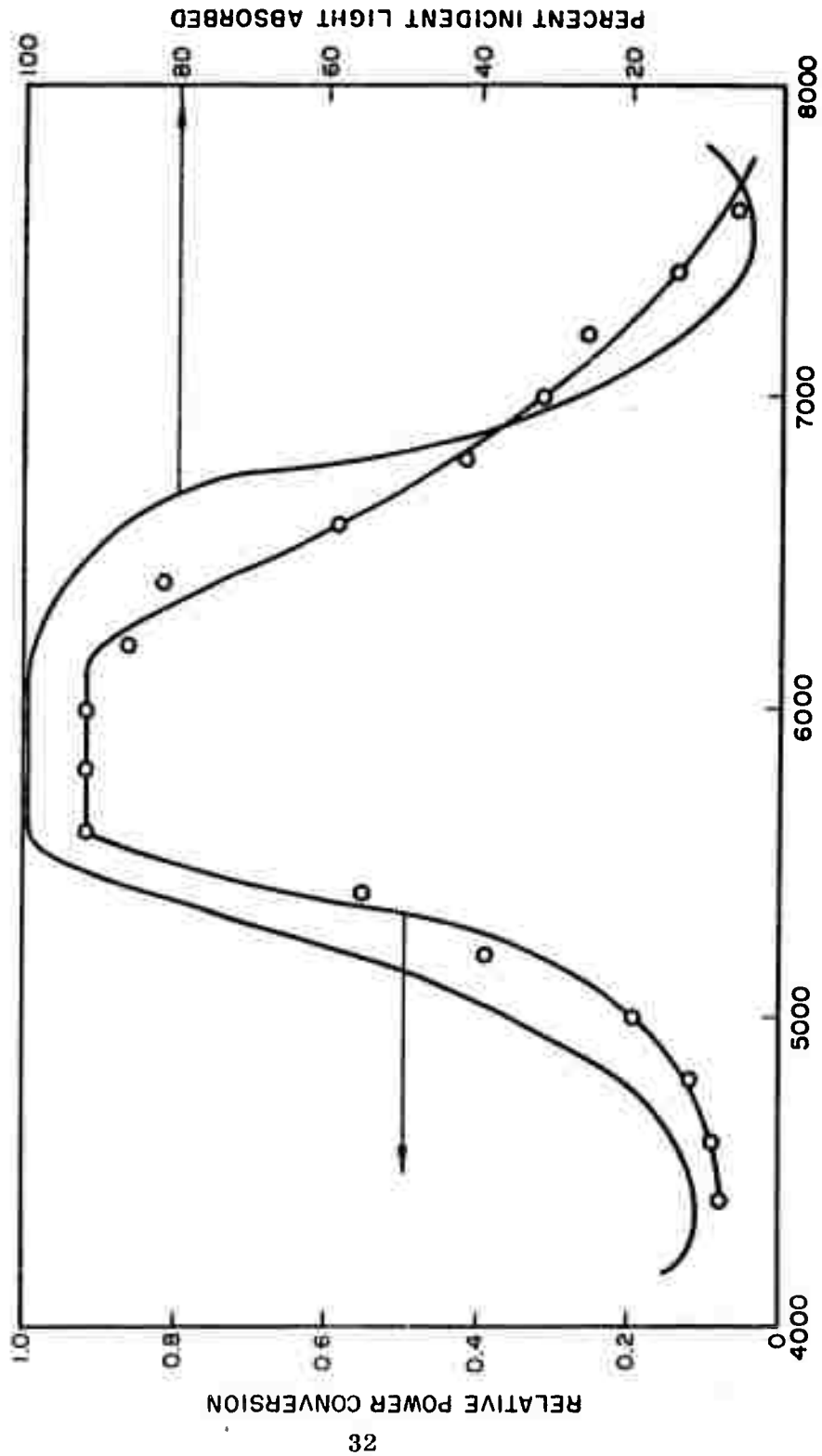


Fig. 10 Spectral Response of Relative Power Conversion

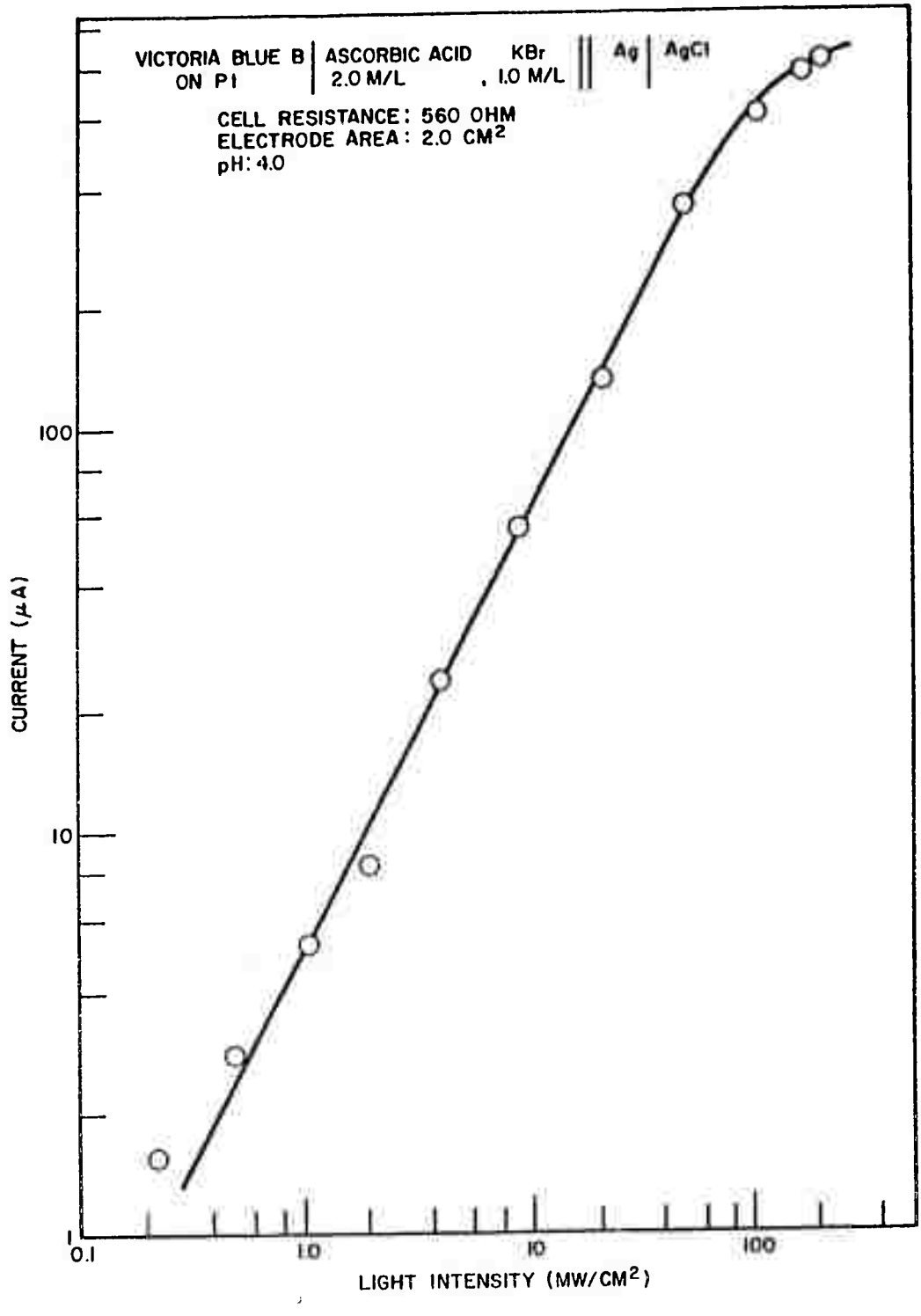


Fig. 11 Limiting Current as a Function of Light Intensity

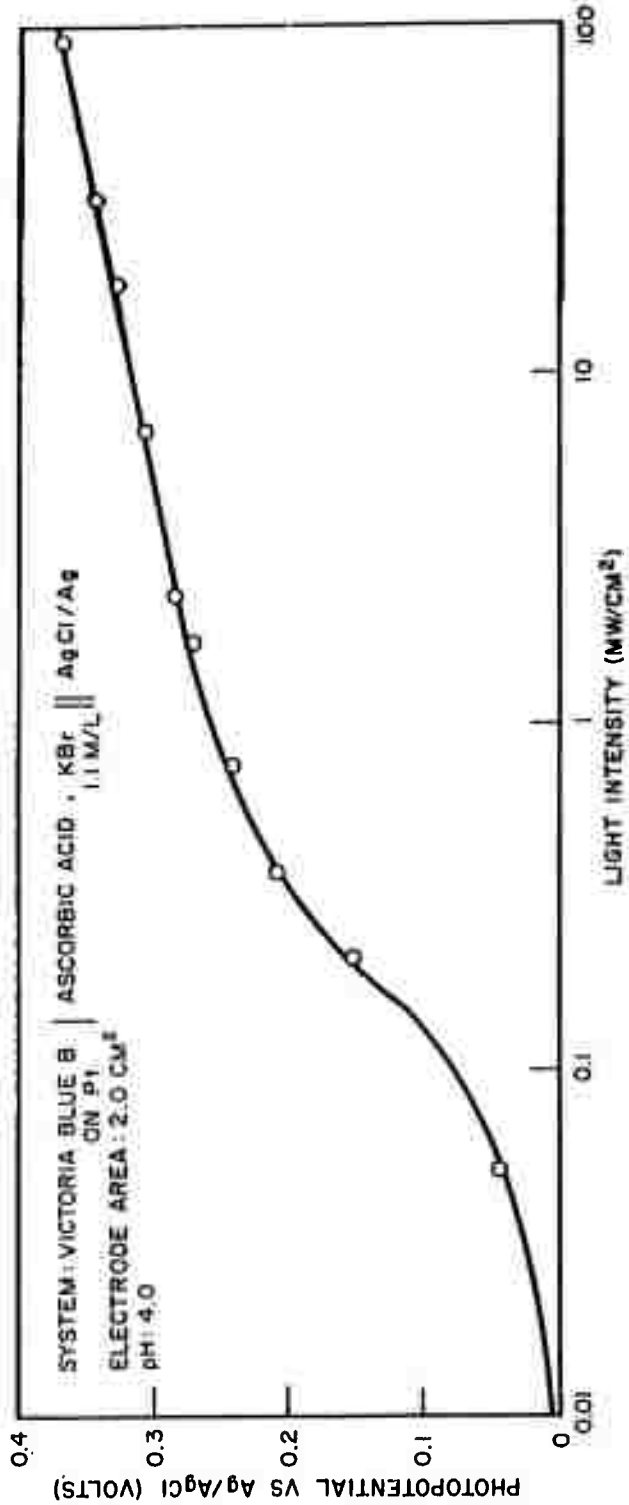


Fig. 12 Photopotential as a Function of Light Intensity

the light intensity. The linear portion between 1 to 100 mw/cm^2 has a slope of 0.055 volts/log I_ϕ. This could be explained by a Nernst-type relationship of the form

$$E = E_0 - \frac{RT}{n} \log I_\phi \quad .$$

where I_ϕ is the light intensity and the other symbols have their usual meaning. In this case, the slope of the straight line plot is $\frac{0.059}{n}$. The actual slope of 0.055 strongly suggests a reaction mechanism involving a 1-electron change as the rate determining step.

Effect of the thickness of the dye coating. It was expected that as the thickness of the dye coating increased a larger percentage of the incident light would be absorbed as was found. However, the quantum yield of electrons defined as

$$\phi_\lambda = \frac{\text{faradays}}{\text{einstein}}$$

at a fixed load and at a wavelength λ of 598 mμ decreased (Fig. 13). This is probably a result of the increased diffusion path.

Miscellaneous dye-coated electrodes. Table 4 lists the results obtained with various dyes deposited on a platinum electrode. The dyes were chosen on the basis of similar structure with known photosensitive materials and water insolubility. All of the dyes except Sulfon Cyanine Blue G developed appreciable photopotentials with an ascorbic acid electrolyte. However, only Aniline Blue, Victoria Blue R, and Victoria Blue B developed appreciable photocurrents. This does not imply that the other dyes would not be able to develop appreciable photocurrents with other reducing agents.

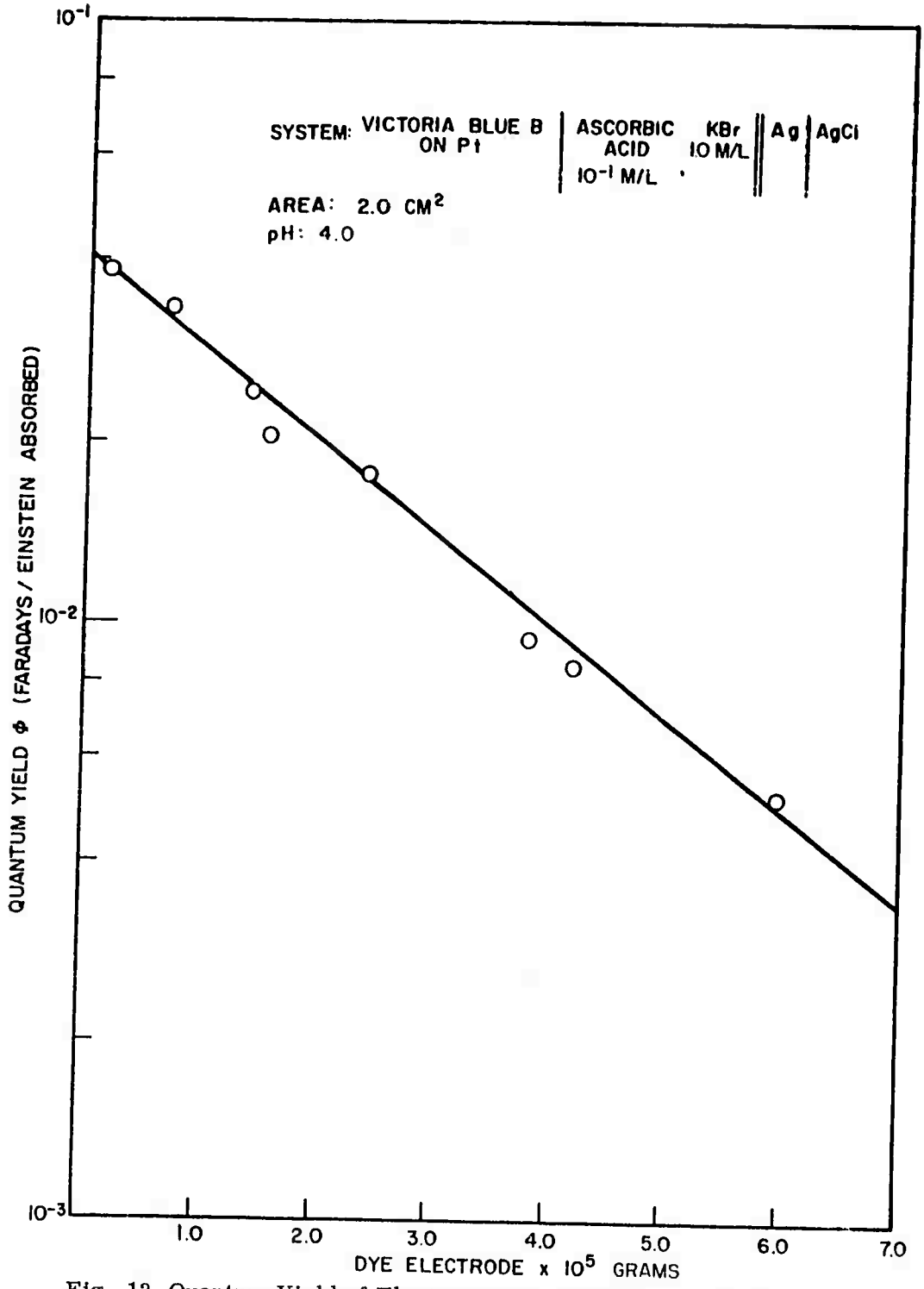


Fig. 13 Quantum Yield of Electrons as a Function of Dye Coating Thickness

Table 4

MISCELLANEOUS DYE-COATED ELECTRODE SYSTEMS

Dye	Reducing Agent	Reducing Agent Concentration (M/l)	E_{Dark} (a) (v)	E* (a) (v)	ΔE (v)	pH	Current (b), (c) (μa)
Pinacyanol	Ascorbic Acid	0.1	+0.023	-0.330	0.353	4	7
Pinacyanol	Ascorbic Acid	0.1	+0.012	-0.290	0.302	4	1
Aniline Blue	Ascorbic Acid	0.1	+0.115	-0.290	0.405	4	45
Aniline Blue	Ascorbic Acid	0.1	+0.080	-0.340	0.420	4	52
Coralline Red	Ascorbic Acid	0.1	+0.095	-0.145	0.240	4	2
Coralline Red	Ascorbic Acid	0.1	+0.105	-0.150	0.255	4	2
Rose Bengal	Ascorbic Acid	0.1	+0.048	-0.160	0.208	4	0
Rose Bengal	Ascorbic Acid	0.1	+0.015	-0.180	0.195	4	0
Victoria Blue R	Ascorbic Acid	0.1	+0.070	-0.325	0.395	4	13
Victoria Blue R	Ascorbic Acid	0.1	+0.065	-0.325	0.390	4	14
Ethyl Eosin	Ascorbic Acid	0.1	+0.114	-0.195	0.309	4	0
Ethyl Eosin	Ascorbic Acid	0.1	+0.133	-0.215	0.348	4	0
Sulfon Cyanine Blue G	Ascorbic Acid	0.1	+0.090	+0.078	0.012	4	
Sulfon Cyanine Blue G	Ascorbic Acid	0.1	+0.083	+0.071	0.012	4	
Victoria Blue B	Ascorbic Acid	0.1	+0.120	-0.360	0.480	4	59
Victoria Blue B	Ascorbic Acid	0.1	+0.098	-0.355	0.453	4	75

(a) Potential vs. a silver, silver chloride electrode.
(b) Electrode area: 2 cm^2.
(c) The cell resistance in all cases, except as noted, was between 800 and 1200.

Power experiments. Thus far, the maximum power density of a simple box cell, using 2 M/l of ascorbic acid and Ag/Ag Cl working electrode was 135 $\mu w/cm^2$ at a power input of 62 mw/cm^2. Thus the overall power conversion efficiency was only 0.22 percent. However, it must be remembered that the box cell experiments are far from ideal and a large amount of energy is lost due to internal resistance and reflections. It is estimated that the actual efficiency is greater than 1 percent.

The VBB-coated electrode was assembled in a 2-cell regenerative power system as described in Ref. 3. The schematic diagrams of the cells are

Cell 1

Victoria Blue B (Pt)	Ascorbic Acid 0.01 M/l	Sn^{++++} 0.04 M/l	Sn^{++} 0.04 M/l	KF 0.5 M/l		Pt

Cell 2

Pt	Ascorbic Acid 0.01 M/l	Sn^{++++} 0.04 M/l	Sn^{++} 0.04 M/l	KF 0.5 M/l	Pt

In Cell 1, termed the regenerator because it is in this cell that the photoinduced reaction takes place, the electrode reactions are the production of dehydroascorbic acid and stannous ion. In Cell 2, the dehydroascorbic acid is reduced to ascorbic acid and the stannous reoxidized to stannic ion. This system operated for three months with a constant current drain of over 50 μa from the dark cell (Cell 2) during light and dark cycles. A cycle consisted of 20 min of light and 40 min of darkness. Current was drawn from the regenerator (Cell 1) only during the light cycle.

Initially, this system developed a photopotential of 0.330 volts. The open-circuit voltage in the regenerator was 0.180 volts and in the fuel cell 0.150 volts. Current-potential curves for the fuel cell and the regenerator are shown in Figs. 14 and 15.

Fig. 14 Electrode Potential and Cell Voltage of the Regenerator as a Function of Current

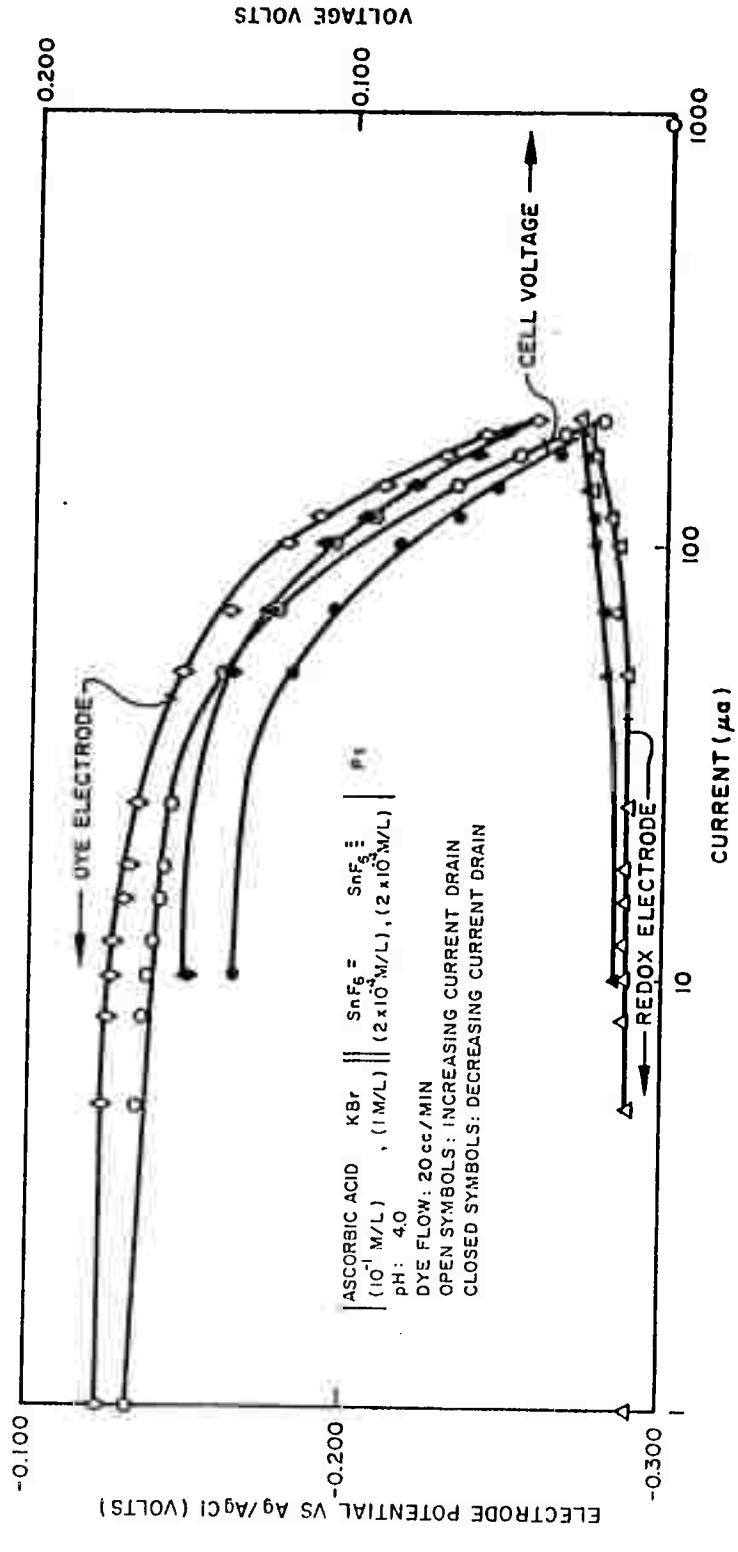


Fig. 15 Electrode Potential and Cell Voltage of the Fuel Cell as a Function of Current

After 43 days of cycling, the regenerator was able to deliver 185 μa and operate at a power density of 6.9 μw while the fuel cell delivered 75 μa and operated at a power density of 3.45 $\mu w/cm^2$.

4.2.2 Soluble Dye Systems

Because of the decided advantages of dye-coated electrodes, a gradual phase out of the investigation of water-soluble dyes was started. The study of soluble dye systems has served to establish the fundamental feasibility of the approach and to elucidate some of the technical and operational problems involved.

Experimental procedures. Quantum efficiencies of photobleaching were obtained by measuring the change of transmittancy per unit time when the system was illuminated by monochromatic light. The light source was the usual Bell & Howell projector passed through a 443 mμ interference filter for monochromaticity. The transmitted light was passed through a Bausch & Lomb grating monochromator (33–86–40) to filter out the fluorescent light. The intensity of the incident light I°_{ϕ} was measured with a calibrated Eppley thermopile. The Lucite cells had an optical path length of 1 cm. The rates were followed by recording the change in transmittancy per unit time of illumination and calculating the corresponding change in concentration using Beer's law.

The energy absorbed by the dye is calculated by multiplying the incident energy I°_{ϕ} by the fraction of energy absorbed

$$A_o = (1 - T)$$

where T is the fraction of light transmitted

$$T = \frac{I_{\phi}}{I^{\circ}_{\phi}}$$

where I_{ϕ} is the transmitted light and I°_{ϕ} is the incident light.

Therefore,

$$A_o = 1 - \frac{I_\phi}{I^\circ_\phi}$$

The quantum efficiency is defined by the relation

$$-\frac{dc}{dt} = I_\phi^{abs}\ \phi$$

where $\frac{dc}{dt}$ is the rate of change of concentration, I_ϕ^{abs} is the energy absorbed, and ϕ is the quantum efficiency. By definition

$$I_\phi^{abs} = I^\circ_\phi - I_\phi$$

or

$$I_\phi^{abs} = I_o\left(1 - \frac{I_\phi}{I^\circ_\phi}\right)$$

Therefore

$$I_\phi^{abs} = I_o\ A_o$$

and

$$\phi = \frac{-\frac{dc}{dt}}{I^\circ_\phi A_o}$$

The limiting factor in the power conversion efficiency of the proflavine ascorbic acid appears to be the rate of photobleaching. Since the rate is known to be most rapid at pH 4 (Ref. 15), studies were made on the use of additives to increase the rate at this pH.

The most effective means of increasing the rate of the photochemical reaction would be to enhance the rate of the singlet to triplet state transition (Ref. 15). It has been

reported (Refs. 16, 17, and 18) that atoms of high atomic number will enhance this transition by both intermolecular (Refs. 16 and 17) and intramolecular (Ref. 18) processes. For example,it was shown (Ref. 18) that in halo-substituted aromatic hydrocarbons the excited singlet to triplet radiationless transition is enhanced. The order of effectiveness was found to be I > Br > Cl > F. This phenomenon has been interpreted as an external perturbation of the spin orbit coupling in the π electron orbitals. The atomic number of the perturbing atom is accepted as the fundamental parameter for correlation of the perturbing effect, i.e., the larger the atomic number the greater is the effect.

The intermolecular effect has been demonstrated (Refs. 16 and 17) with ethyl iodide. In this case, the process was interpreted as a collisional perturbation of the spin orbit coupling in the π electron orbits. This perturbation is not a result of formation of strong complexes or diffusion controlled encounters, but rather a result of repeated collisions within a solvent cage or energy trap within the solvent.

Applying this case to the proflavin-ascorbic acid system, the effect of added halide salts on the rate of photobleaching was studied. As shown in Table 5, with the exception of potassium iodide, the rate increases as expected. It is suspected that KI is photochemically oxidized to iodine where it reacts with the bleached dye to reoxidize it to the colored form. The effect of concentration is more or less as expected; the rate increases to a maximum and levels off.

Table 5

THE EFFECT OF ADDED HALIDE SALTS ON THE RATE OF PHOTOBLEACHING IN THE PROFLAVIN-ASCORBIC ACID SYSTEM[a]

Salt	Concentration (M/l)	Relative Rate[b]
KF	0.1	1.0 ± .03
KCl	0.1	1.25 ± .02
KBr	0.1	2.3 ± .01
KI	0.1	1.1 ± .05
KBr	0.01	1.4 ± .02
KBr	1.0	3.9 ± .01
KBr	1.5	3.5 ± .01

(a) Solutions buffered with biphthalate at pH 4.
(b) Rate in absenee of added halide taken as 1.0.

Effeet of dye eoneentration. A study was made of the effect of increased dye eoneentration on the quantum efficiency of photobleaching. It was first determined that Beer's law held up to and including a 2×10^{-4} M/l proflavin solution. The quantum efficiency of photobleaching of a 2×10^{-4} M/l solution was found to be 1×10^{-2} M/einstein. This is in agreement with Millich (Ref. 15) who reported that quantum efficiencies of a similar system increased with dye concentration to a value of about 1×10^{-2} M/einstein at a eoneentration of 2×10^{-5} M/l where the efficiency leveled off.

Regenerative systems using proflavin-ascorbic acid. Several attempts have been made to operate complete regenerative systems incorporating the proflavin-ascorbic acid system. The most successful system is represented schematically by

Pt	Proflavin 0.0004 M/l	Ascorbic Acid 0.01 M/l	KBr 0.01 M/l	$SnF_6^{=}$ 0.04 M/l	$SnF_6^{\equiv}$ 0.04 M/l	Pt

A photopotential of 0.05 volts was measured. The illuminated cell or regenerator delivered currents of over 200 μa while the dark cell (fuel cell) delivered currents in excess of 30 μa. The maximum power density obtained from the illuminated cell was 0.5 $\mu w/cm^2$. This system was operated successfully for five weeks.

4.2.3 Inorganic Complexes

Photosensitivity of Werner-type complexes is well known although only a few quantitative observations have been reported (Refs. 19 and 20). Recently, Adamson and Sporer (Ref. 21) reported on the photochemical reactions of some aqueous complexes of Co III on Cr III oxidation states. These compounds were reported to form an excited doublet state which decayed to a metastable quartet, thus forming an analogous system to the excited singlet metastable triplet states of photosensitive dyes, and therefore were considered an interesting subject for further study.

Experimental procedures. The Werner type salts were prepared according to literature procedures:

- $Co(NH_3)_6(NO_3)_3$ by the method of Wendt and Jander (Ref. 22). The compound is a yellow crystalline material.
- $[Cr(NH_3)_5Cl]Cl_2$ by the method listed in Inorganic Synthesis (Ref. 23).
- Cis - $[Cr(en)_2Cl_2]Cl \cdot H_2O$ also by a method from Inorganic Synthesis (Ref. 24). The latter compound polymerized and it was not possible to obtain in a crystalline form.

These compounds were tested for photogalvanic properties in the same manner as the organic dyes (Ref. 3).

Results. The three compounds listed above were tested for photogalvanic effects with a variety of reducing agents. As can be seen from the results listed in Table 6, large photopotentials were obtained with chromium pentammine complex. However these systems proved to be irreversible in the absence of oxygen. Further there was evidence,

Table 6

PHOTOPOTENTIALS OF COMPLEX ION-REDUCING AGENT SYSTEMS

Table 6
PHOTOPOTENTIALS OF COMPLEX ION-REDUCING AGENT SYSTEMS

Complex[a]	Reducing[b] Agent	Dark Potential[c] E_{dark} (v)	Photoinduced Potential[c] E(v)	Photo-Potential E-E dark (v)	pH	Remarks
Cis $Cr(en)_2 Cl_2 Cl$	ascorbic acid	-0.054	-0.106	-0.052	4	very reversible
$Cr(NH_3)_5 Cl Cl_2$	ascorbic acid	-0.198	-0.243	-0.045	4	ppt.
	disodium ethylene-diamine tetra-acetate	-0.032	-0.075	-0.043	7	irreversible
	ascorbic acid-F^{++}	-0.015	-0.053	-0.038	7	irreversible
	ascorbic acid	-0.060	-0.122	-0.062	7	slightly reversible
	Fe^{++}	-0.144	-0.256	-0.112	6	ppt.
	hydroquinine	+0.165	-0.035	-0.200	7	slightly reversible
	Fe^{++}-hydroquinine	+0.212	+0.011	-0.201	7	slightly reversible
	Fe^{++}	+0.140	-0.068	-0.208	7	irreversible
	Fe^{++} & trace ascorbic acid	-0.036	-0.290	-0.254	7	irreversible
$Co(NH_3)_6(NO_3)_3$	EDTA	+0.263	+0.263	-0.0	4	
	Fe^{++}	+0.165	+0.165	0.0	4	
	ascorbic acid	-0.040	-0.040	0.0	4	
	Fe^{++}	+0.244	+0.260	-0.034	2	irreversible
	Fe^{++}	-0.017	-0.054	-0.037	6	irreversible
	EDTA	+0.205	+0.209	-0.096	6	irreversible

(a) concentration were 0.014M, (b) concentrations were 0.01M, (c) all potentials measured vs Ag/AgCl reference electrode.

demonstrated by a color change upon prolonged illumination, that the complexes were being disrupted by the light.

It is of interest to note that the $[Cr(NH_3)_5Cl]Cl_2$ complex changed from pink to green and the $Co(NH_3)_6(NO_3)_3$ changed from yellow to pink, the colors, respectively, of the hydrated Cr (III) and Co (III) ions. Since the platinum electrode in contact with these solutions became more negative upon illumination, it is apparent that the central atoms of the complexes are undergoing a photochemical reduction and are subsequently reoxidized at the electrode.

Since it did not appear likely that a regenerative system based on this class of compounds could be developed, further work was abandoned.

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Section 5
CONCLUSIONS

5.1 TASK A, THERMALLY REGENERATIVE SYSTEM

Cadmium, iodine fuel cells operated at 418°C have delivered power densities of 56 mw/cm^2 at the anode and 126 mw/cm^2 at the cathode.

The open-circuit voltage and polarization decrease with increasing temperature, thus the optimum operating temperature is a function of current density.

The change of open-circuit cell voltage with temperature, $\Delta V_r/\Delta T$, was found to be 0.46 mV/°K, corresponding to a ΔS of -21.2 eu over the temperature range 380°C to 520°C.

The applied pressure of iodine was found to have no effect on the anode but to be beneficial to the cell voltage and cathode polarization as the pressure was increased. The optimum pressure is a function of porosity and pore size distribution of the gas diffusion electrode.

The electrolyte composition was found to have very little effect if the mole percent of cadmium iodide is kept between 60 and 75 percent.

5.2 TASK B, PHOTOCHEMICALLY REGENERATIVE SYSTEMS

Dye-coated electrodes were found to have some important advantages over soluble dye systems. The coated electrodes reacted more rapidly to changes from light to dark and current densities of an order of magnitude higher (200 μa/cm^2) were achievable.

Victoria Blue B, used for most of the investigation with coated electrodes, has a broad absorption band capable of absorbing about 40 percent of the incident solar energy on the earth's surface.

A free energy change of 40.8 kcal was calculated for the activation energy. The photopotential was found to be a function of the oxidation-reduction potential of reactive species in the electrolyte in contact with the coated electrode. The photopotential averages about 0.450 volts or 10.4 kw or about a 25 percent efficiency.

The current was found to increase with increasing temperature as a result of an increase in the conductivity of the electrolyte of the cell.

The temperature coefficient of the photoinduced potential $\frac{\Delta E^{\circ}_{*}}{\Delta T}$ at open circuit is 1.2 mv/°K corresponding to a ΔS of -55 eu. The theoretical efficiency of the electrochemical reaction was calculated to be 55 percent.

Assuming 40 percent of the incident energy is absorbed, the overall efficiency is about 5.5 percent if the fuel cell is operated without polarization losses. The electrode potential of dye-coated electrodes was found to be independent of wavelength and a logarithmic function of light intensity.

The limiting current was found to be dependent upon both the wavelength and intensity. The dependency on wavelength follows closely the absorption spectrum of the dye.

Quantum efficiencies were found to vary inversely with the thickness of the dye coating.

Dye-coated electrodes have, in rather crude experiments, shown a 0.22-percent power conversion efficiency and have been operational in a regenerative system for 3 months delivering current constantly at a level of 50 μa and intermittently, during light cycles at 200 μa.

The rate of photobleaching of soluble dyes was shown to be considerably enhanced by the addition of alkali metal halides.

Inorganic complexes of the Werner type are photosensitive, but apparently the irreversibility of the reaction makes these compounds unsuitable for use in regenerative systems.

Section 6
PROGRAM FOR NEXT INTERVAL

6.1 THERMALLY REGENERATIVE SYSTEMS

The program for the next interval will be divided into three phases.

Phase 1 is a continuation of the fuel cell study. The effect of electrode preparation on the properties of the cathode will be considered. Lifetime and faradaic efficiencies will be evaluated. This program depends upon the successful construction of a fuel cell, which will have low resistivity and is gas tight.

Phase 2 will consider the problem of regeneration. This problem may in practice be separated as follows:

- Decomposition of Cd I_2
- Separation of the Cd and I_2

The study of the decomposition will be concerned with evaluating the following:

- Temperature and pressure coefficients of the equilibrium constant
- Temperature and pressure coefficients of the rate constants
- Effect of flow rates
- Catalytic effect, positive or negative, of possible materials of construction of the walls of the reactor. This will include impregnating the walls with possibly catalytic active materials.

A major effort will be made in this area to obtain data on the decomposition of Cd I_2 as soon as possible. The major problem continues to be the design of an apparatus, which will permit the required measurements and still withstand the thermal shocks and corrosive materials involved.

The study of the separation will of necessity include the evaluation of the rate of recombination of the Cd and I_2 to form Cd I_2 as a function of temperature, pressure, and flow rate.

Separation by quenching, by thermal diffusion, and by sudden expansion of gas through a throttling value will be evaluated.

Phase 3 will consider the engineering and design studies. The problems to be considered are described below:

- Compression of the iodine for delivery to the cell under pressure
- Materials of construction
- Circulation of the materials, gaseous iodine, molten salt, and liquid Cd
- Design of a complete regenerative system and multiple cells

6.2 PHOTOREGENERATIVE SYSTEMS

This program, to be phased out by 1 Sept 1961, will be concerned with completing some of the exploratory program on photosensitive elements and reducing agents and elucidation of the mechanism of the photoinduced reactions.

The exploratory program will evaluate

- Chlorophyll deposited on an electrode or dissolved in a nonaqueous solvent
- Organic materials in the flavine and polyacene class. Materials in these classes are water insoluble and have been reported to be photoactive.
- Inorganic semiconductor

Mechanism studies will be conducted by measuring the change in current, which is a function of the overall rate of reaction, as a function of temperature diffusion path lengths in liquid and, in the case of solid photosensitive elements, also in the solid. The effect of temperature on the dark current, which is a measure of the energy of

activation of the dead reaction, will be correlated with the threshold energy of the photoinduced reaction, which is a measure of the energy of activation of that reaction.

An attempt will be made to establish a unified theory explaining the various phenomena uncovered in this study.

A complete regenerative system incorporating a fuel cell and regenerator will be assembled using the optimum conditions as they are now known.

Section 7
IDENTIFICATION OF PERSONNEL AND DISTRIBUTION OF HOURS

Personnel assigned to this project and the approximate number of hours of work performed by each are as follows:

	Hours
H. Silverman	500
S. Greenberg	960
W. Momyer	960
R. Wales	800
L. Williams	800
Miscellaneous hourly	500
	4520

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